THE ORGANIC STOICHIOMETRY OF THE KHARASCH REACTION

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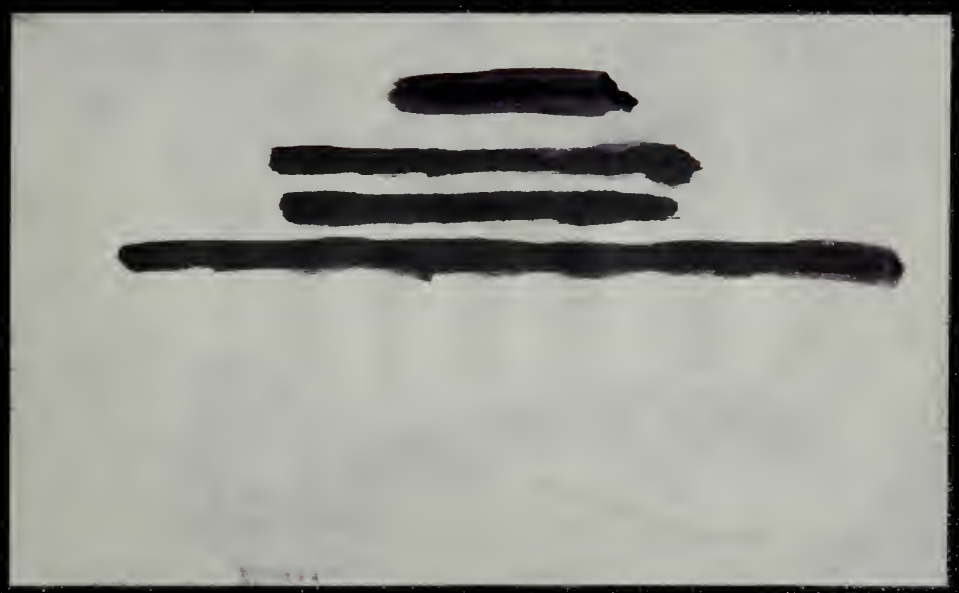

THE ORGANIC STOICHIOMETRY OF THE KHARASCH REACTION

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ABSTRACT

The reaction between hexylmagnesium bromide and hexyl bromide, catalyzed by cobaltous bromide is studied in ether and in tetrahydrofuran. The corresponding reaction of amyl Grignard in ether is also studied. Analysis of organic products was by gas partition chromatography and by titration of hydrolyzed Grignard. The observations are discussed relative to prior work, particularly noting the significance of the physical state of the catalyst and the nature of the organic moeity.

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1. Introduction

The reaction between Grignard reagents and organic halides catalyzed by cobaltous halides has been known since 1915. Much interest has centered on this reaction for its utility in yielding coupling products as well as search for its mechanism. The foremost investigator has been the late M. S. Kharasch,[1] who proposed a mechanism involving a cobalt subhalide.

A study of the product distribution of the Kharasch reaction was made with the hope of a better understanding of reaction conditions versus product yield. Amyl and hexyl Grignard were reacted with their respective organic halides with the aid of cobaltous bromide in diethyl ether and in tetrahydrofuran (THF). Samples were analyzed before and after catalyst addition by gas partition chromatography and by the standard titration method. The observations are discussed relative to prior work particularly noting the significance of the physical state of the catalyst and the nature of the organic moeity.

[1] M. S. Kharasch and O. Reinmuth, Grignard Reactions of Non-metallic Substances, Prentice-Hall, 1954.

2. Historical

The reaction between a Grignard reagent and an organic halide first came to light in 1912 when Jolibois reported[2] finding ethane and ethylene as products of an unwanted side reaction in the synthesis of ethylmagnesium iodide from ethyl iodide. Three years later Kondyrew and Fomin reported[3] the same reaction under cobaltous chloride catalysis. Several workers studied this catalyzed reaction, for its own sake and as a preparative route.[4,5] M.S. Kharasch at the University of Chicago investigated this and similar reactions[6] so extensively that the reaction now bears his name. The Kharasch Reaction is the reaction between Grignard reagent and an organic halide that is catalyzed by halides of Group VIII metals, primarily cobaltous halides. The products can be due to dimerization and/or disproportionation.

$$RMgX + R'X \xrightarrow{CoX_2} R\text{-}R \text{ (and/or } R^1R,\ R'\text{-}R') + MgX_2$$

and/or

$$2RMgX + 2R'X \xrightarrow{CoX_2} {}^{R}(H+) + {}^{R}(H-) + {}^{R'}(H+) + {}^{R'}(H-) + 2MgX_2$$

[2]Jolibois, Compt. rend., 155, 213 (1912), cited by C.B. Linn and C.R. Noller, J. Am. Chem. Soc., 58, 816-9 (1936).

[3]Kondyrew and Fomin, J. Russ. Phys.-Chem. Soc., 47, 190-8 (1915), cited by M.S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice-Hall, New York, 1954, p. 137.

[4]M.S. Kharasch, J.S. Sallo, and W. Nudenberg, J. Org. Chem., 21, 129-135 (1956).

[5]W.B. Smith, J. Org. Chem., 26, 4206-9 (1961).

[6]Kharasch and Reinmuth, loc. cit.

Kharasch proposed a working hypothesis[7] illustrated by the following equations:

$$RmgX + CoX_2 \longrightarrow RCoX' + X'MgX$$

$$2RCoX' \longrightarrow R\text{-}R + 2 \cdot CoX'$$

$$2RCoX' \longrightarrow R_{(H+)} + R_{(H-)} + 2 \cdot CoX'$$

$$RCoX' \longrightarrow \cdot R + \cdot CoX'$$

$$R'X'' + \cdot CoX' \rightarrow \cdot R' + X''CoX'$$

The fate of organic free radicals in solution will depend upon the nature of the radical and the system. Kharasch gives four possibilities:

$$\cdot R' + (C_2H_5)_2O \longrightarrow R'H + \cdot HC(OC_2H_5)CH_3$$

$$\cdot R' + RMgX \longrightarrow R'H + R_{(H-)} + \cdot MgX$$

$$\cdot R' + RMgX \longrightarrow R'\text{-}R + \cdot MgX$$

$$2 \cdot R' \longrightarrow R'_2$$

Kharasch advanced no evidence for the existence of a cobaltous subhalide, but he was quite convinced that the reaction takes place via free radicals.[8,9]

Wilds and McCormack proposed an alternative reaction scheme,[10] which they believed more closely fit the observation that the intermediate retained its catalytic properties for a relatively long period

[7]Kharasch and Reinmuth, op. cit., pp. 123-4.

[8]M.S. Kharasch and W.H. Urry, J. Org. Chem., 13, 101-9 (1948).

[9]M.S. Kharasch, J.K. Hambling and T.P. Rudy, J. Org. Chem., 24, 303-5 (1959).

[10]A.L. Wilds and W.B. McCormack, J. Org. Chem., 14, 45-55 (1949).

of time*. Their proposal was a chain mechanism in which cobalt metal (in highly reactive colloidal form) is the reducing agent:

$$2RMgX + CoX'_2 \longrightarrow MgX_2 + MgX'_2 + \{R_2C0\}$$

$$\{R_2Co\} \rightarrow R_{(H+)} + R_{(H-)} + Co$$

$$2R'X + Co \rightarrow CoX_2 + 2\cdot R' \rightarrow R'-R'$$

Slaugh doubted the free radical mechanism[11] and concluded that the interchange reaction between Grignard reagent and organic halide probably determines the reaction products. Slaugh prepared cyclopropane from 3-phenoxypropyl bromide and from the analysis of these data proposed this mechanism:

$$C_6H_5\text{-}O\text{-}C_3H_6\text{-}Br + C_2H_5MgBr \xrightarrow{CoBr_2} C_6H_5\text{-}O\text{-}C_3H_6\text{-}MgBr + C_2H_5Br$$

$$C_6H_5\text{-}O\text{-}C_3H_6\text{-}MgBr \rightarrow C_6H_5\text{-}O\text{-}MgBr + C_3H_6$$

$$C_2H_5Br + C_2H_5MgBr \xrightarrow{CoBr_2} C_2H_4 + C_2H_6 + MgBr_2$$

Lee and Thornhill[12] found little isotope (^{14}C) rearrangement in the reaction between Grignard reagent and 2-phenylethyl bromide catalyzed by cobaltous bromide.

Davies, Hey, and Tiecco[13] successfully trapped aryl radicals by the slow addition of an ethereal solution of methylmagnesium iodide to a benzene solution of p-bromotoluene in which $CoBr_2$ was suspended. Identification of 4-methylbiphenyl (16% yield) in the product mixture

*longer than ·CoX' would be expected to exist as such.

[11] L.H. Slaugh, J. Am. Chem. Soc., 83, 2734-9 (1961).

[12] C.C. Lee and D.P. Thornhill, Can. J. of Chem., 42, 1502-6 (1964).

[13] D.I. Davies, D.H. Hey, and M. Tiecco, J. Chem. Soc., 1965, 7062-71.

clearly indicated that p-tolyl radical, derived from the halide, was an intermediate in the reaction. From a study of isomer ratios of monosubstituted biphenyls obtained from Kharasch reactions, Davies and coworkers further concluded that the species which attacks the halide has a larger size than that of a phenyl radical. And finally, "Thus the possibility of the attacking radical's being complexed with ether and/or either cobalt or cobaltous chloride or some other metallic or organometallic species must be regarded as possible."

Costa, Mestroni, and Boscarato[14] have recently isolated a complex which fits Davies' description. These researchers reacted dimesitylmagnesium bromide and $CoBr_2$ in THF and obtained a yellow-green precipitate, which gave dimesityl upon thermal decomposition. They report the precipitate as having the formula $[C_6H_2(CH_3)_3]_3Co.C_6H_2(CH_3)_3MgBr.THF$. Costa and coworkers further propose that the organocobalt intermediate involves cobalt in a zero oxidation state which may help explain the oxidation-reduction situation without the earlier discussion[10] regarding highly reactive cobalt metal as an intermediate.

All of the mechanisms have been presented without distinguishing between aliphatic and aromatic systems. This distinction should be made because of the inability of aromatic fragments (eg. phenyl radical) to disproportionate. The mechanism remains unsettled.

In attempting to understand the stoichiometry of the Kharasch reaction, attention should be paid to the nature of the reactants and solvent, and whether the reaction is homogeneous or heterogeneous. A survey of the literature shows that most reports of the Kharasch reaction do not state whether the catalyst is in suspension or is dissolved in

[14] G. Costa, G. Mestroni, and G. Boscarato, La Ricerca Scientifica, Rend. A 7 (2) 315-22 (1964).

the solvent. A sizable yield should not necessarily be attributed to the catalyst. For example, Soroos and Willis reported[15] a 43% yield of coupling product in the reaction between t-amyl chloride and n-propylmagnesium chloride without the aid of cobaltous halides. The latter does not always alter the extent of the reaction. Kharasch and coworkers found[16] no additional coupling of phenylmagnesium bromide to give biphenyl with the aid of cobaltous chloride. On the other hand, the effect of the catalyst can be quite pronounced. In one of the few papers which report analysis of products before and after catalyst addition, Kharasch and co-workers[17] found that the extent of reaction of bornyl chloride with methylmagnesium bromide increased from 5% to 98% upon the addition of cobaltous chloride*.

Predicting the stoichiometry of the Kharasch reaction can be difficult. Wilds and McCormack[10] obtained a 58% combined isomer yield of coupled ether when 1-(p-methoxyphenyl) propyl bromide reacted with ethereal ethylmagnesium bromide in the presence of cobaltous bromide. Analyses for low boiling hydrocarbons were not conducted; the reaction was stated as heterogeneous. Apparently conflicting results were reported by Kharasch, Stampa, and Nudenberg[18] who reacted n-hexyl bromide

[15] H. Soroos and H. B. Willis, J. Am. Chem. Soc., 63, 881 (1941).

[16] M. S. Kharasch, D. W. Lewis and W. B. Reynolds, J. Am. Chem. Soc., 65, 493-5 (1943).

[17] M. S. Kharasch, F. Engelemann and W. H. Urry, J. Am. Chem. Soc., 66, 365-7 (1944).

[18] M. S. Kharasch, G. Stampa, and W. Nudenberg, J. Org. Chem. 18, 575-81 (1953).

* It is unclear whether the catalyst was added in the solid phase, or in solution.

with catalyzed i-propylmagnesium bromide in ether. On the basis of Wilds and McCormack's findings, one would expect to obtain the coupled product from the halide, i.e., n-dodecane. Kharasch and coworkers found no dodecane, but instead detected hexane, hexene and a small amount of 2-methyl octane. Again catalyst condition was not stated and one wonders whether a homogeneous reaction might explain the lack of dodecane.

Much remains confused in the mechanism, reaction conditions, and stoichiometry of the Kharasch reaction.

3. Experimental

Reagents

Amyl bromide (Eastman Kodak Company) was redistilled on a gold-plated Monel spinningband column. Refractive index 1.4422 at 25°C. (Lit: 1.44199).[19] Analysis of distillate on the gas chromatograph (GPC) revealed no foreign peaks.

Hexyl bromide (Matheson, Coleman and Bell) was used without further treatment. Refractive index 1.4471 at 25°C. (Lit: 1.44781 at 20°C.).[20] No contaminants were shown upon checking by GPC.

Magnesium turnings (99.8%, J.K. Baker Chemical Co.) were washed with ether and dried for at least 2 days at 105°C.

Cobaltous bromide ($CoBr_2$) was prepared by adding HBr Gas to a water suspension of cobaltous carbonate (Baker and Admason), stripping most of the solvent under vacuum and drying the resulting green $CoBr_2$ at 110°C for two days.

The Grignard Reagent

A 500 ml. three-necked flask was fitted with a water-cooled condenser, stirrer with teflon paddle, and a pressure-equalizing dropping funnel. The reaction was carried out with a positive pressure of Matheson Prep. Grade nitrogen in the system. One gram of

[19] B. J. Mair, Journal of Research of the National Bureau of Standards, Washington, D.C. 9, 457-72 (1932).

[20] Handbook of Chemistry and Physics, (The Chemical Rubber Co., 45 ed.), page C-356.

freshly cut magnesium turnings was introduced into the flame-dried flask. A solution of 1.8 g. alkyl halide in 10 ml. solvent was added in one portion from the dropping funnel and the stirrer started. As soon as the reaction had begun, as determined by formation of cloudiness or condensate, the remaining 100 ml. of solvent was added at the rate of about 15 ml./min. The reaction was allowed to subside and cool to room temperature.

A 100 ml. jacketed reaction vessel, flushed with nitrogen, was maintained at $20.5^{\circ}\pm.2^{\circ}C$. Nitrogen pressure was used to pump the fresh Grignard through glass tubing fitted with a plug of glass wool into the reaction vessel. The cobaltous bromide was added in one portion (solution or solid. . . see Table II) and the system mixed with a magnetic stirrer. Samples were withdrawn with a 5 ml. automatic pipette and hydrolyzed with dilute HCl.

The product mixture was analyzed on an Aerograph Model 600C gas chromatograph employing a 10 ft. by 1/8 in. column packed with 20% QF-1 on 60/80 DMCS Chromosorb W and hydrogen flame detector. Peaks were identified by adding a small quantity of an authentic reagent and noting that the area under the peak in question increased. In the THF system 5 ml. of toluene (2 ml. of chloroform for run C6-5) was added to the hydrolyzed Grignard and the resulting organic layer analyzed. In the hexyl case the organic sample was analyzed by GPC and treated with HBr by bubbling the gas through the solution for one minute. The mixture was allowed to stand overnight, was washed with water and again analyzed by GPC. The reduction in the area of the initial hexane-hexene peak was taken as the amount of hexene present.

All GPC runs had a helium flow of 20 ml./min., 50° initial oven temperature and after one minute a temperature increase to $155^{\circ}C$. at

the rate of 35°/min. Retention times were as follows:

pentane	90 seconds
1-pentene	95
hexane, 1-hexene, ether	118
chloroform	153
THF	198
toluene	245
amyl bromide	314
hexyl bromide	315
n-decane	345
n-dodecane	380

The initial concentration (before catalyst addition) of Grignard was determined by adding 5.0 ml. Grignard to 5.0 ml. of 0.456 M HCl and back titrating with 0.0631 M NaOH using phenolphthalein as indicator.

Grignard reagent was made from amyl bromide (run nos. C5) in ether and hexyl bromide (run nos. C6) in ether and in THF. The analysis of the amyl case by GPC showed amyl bromide and decane not sufficiently resolved to permit accurate quantitative data of yields of coupling and disproportionation products. During two yield checks of amyl Grignard (82.5% and 98.3%), 0.4 g. of solid $CoBr_2$ was introduced directly into the three-necked flask (reaction heterogeneous in $CoBr_2$ and Mg.) GPC analyses before and after catalyst addition show substantial reduction of the amyl bromide peak and growth of the decane peak after the catalyst had been added.

During the last hexyl determination (run no. C6-6) a sample drawn at 39.2 minutes after $CoBr_2$ addition was shown to have a Grignard concentration of 0.0617 M. This is to be compared with a Grignard

concentration of 0.0916 M found before the catalyst was added.

The Kharasch reaction was observed to exhibit a wide range of colors. The initial mixture was usually deep brown or black, but sometimes it was a deep blue or green. As the reaction progressed the mixture often turned somewhat milky or the color became less intense.

TABLE I

(a) ANALYSIS OF GRIGNARD BEFORE ADDITION OF COBALTOUS BROMIDE

Run no.	Solvent	Millimoles Reactant (hexyl bromide)	%Yield RMgX	Remaining Hexyl Bromide	n-dodecane	Hexane + 1-Hexene	% Initial Coupling	Notes
C6-2	THF	11.9	Very low (not detm'd)	6.8±1.0	0.10±0.04	0.47±0.05	1.7	
C6-3	THF	13.3	88.6	1.7±0.2	0.62±0.09	7.2±0.6	9.3	(1)
C6-4	$(C_2H_5)_2O$	11.3	82.0	0.38±0.06	0.45±0.07	(4)	8.0	
C6-5	THF	11.6	88.4	3.0±1.1	0.65±0.27	5.0±0.6	11.2	
C6-6	$(C_2H_5)_2O$	14.8	79.5	4.0±0.6	2.1±0.3	13.7±4.1 all hexane	28.4	(2),(3)

(a) All values are in millimoles related to a nominal 100 ml. system.
(1) An unknown peak appeared at 155 seconds retention time in each run; however, a quantitative check was made in only two runs; C6-3:23.8±.9 mg. and C6-4:14.6±3.0mg.,(same sensitivity as hexane assumed.)
(2) Additional analysis on a Beckman GC-4 GPC using SE-30 column gave separation of hexane, hexene, and ether, which was not accomplished on the Aeograph 600-C GPC. No hexene was found in this sample.
(3) Material balance totals 148% due primarily to substantial evaporation of the solvent on a hot day. Percent initial coupling reported is consequently too high.
(4) Not separated from the ether peak.

TABLE II

(a) ANALYSIS OF GRIGNARD AFTER CATALYSIS

Run No.	Amount & phase of $CoBr_2$ added	Time from $CoBr_2$ add'n. (minutes)	Hexyl Bromide	n-Dodecane	Hexane + 1-Hexene	Notes
C6-2	0.33 millimoles in THF sol'n (2 ml.)	24.1	8.4 ± 0.8	0.12 ±0.03	0.52±0.05	(1)
C6-3	0.42 millimoles in THF sol'n (2 ml.)	23.9	1.74± 0.09	0.62±0.04	4.9±0.2	(1), (2)
C6-4	0.0447g. in 35 ml. ether (decanted)	2.0	0.8±0.2	0.4±0.1	(3)	(1)
C6-5	0.50 g. solid	1.6	3.4±0.3	0.60±0.10	8.4±2.2	
C6-6	0.244 g. solid	17.6	4.7±0.3	2.0±0.2	hexane: 12.0±0.5 hexene: 0.8±0.4	

(a) All values are in millimoles related to a nominal 100 ml. system.
(1) Corrected for dilution effects when solution of catalyst added.
(2) Heterogeneous in magnesium.
(3) Not separated from the ether peak.

TABLE II (continued)

Run No.	Time from $CoBr_2$ add'n. (minutes)	Hexyl Bromide	n-Dodecane	Hexane+ 1 Hexene	% Coupling due to Catalyst	Notes
C6-2	-	-	-	-	0.0	
C6-3	-	-	-	-	0.0	
C6-4	10.6	0.96±0.05	0.4±0.3	(3)	0.0	(4)
C6-5	33.5	4.4±1.4	0.7±0.2	7.2±1.9	0.0	
C6-6	33.3	5.7±1.2	2.2±0.5	0.0	0.0	(5)

(3) Not separated from the ether peak.
(4) A third portion, after 31.9 minutes total time gave 0.84±0.05 hexyl bromide, 0.46±0.03 n-dodecane.
(5) At 23.0 minutes added 0.6 grams of magnesium, and at 33.3 minutes drew a sample.

TABLE III

(a) ANALYSIS AFTER HYDROGEN BROMIDE TREATMENT

Run No.	Hexyl Bromide	n-Dodecane	Hexane	Decrease in combined Hexane/ene peak	Percent Disproportionation
C6-3, before $CoBr_2$	2.4 ± 0.2	0.67 ±0.05	6.4±0.5	0.8±1.1	12.0
C6-3, after $CoBr_2$	2.4 ± 0.2	0.67±0.05	5.5±0.3	(-.6)	--
C6-5, before $CoBr_2$	2.5 ±0.2	0.12±0.06	2.1±0.5	2.9±1.1	50.0
C6-5, after $CoBr_2$ (last sample)	2.7 ± 0.4	0.35±0.05	3.7±0.2	3.5±2.1	60.4

(a) All values are in millimoles related to a nominal 100 ml. system

4. Discussion.

In 1964 Whittaker[21] made a kinetic study of the Kharasch reaction using amyl Grignard, the corresponding organic halide, and cobaltous bromide. By drawing samples of the reaction mixture at timed intervals and titrating them, he obtained data of Grignard concentration versus time. A plot of these variables consistently showed that the Grignard concentration went through a minimum, rose to a maximum and then tapered off. No coupling product was found by GPC. The present work was undertaken in the hope of identifying the "hump" in the plot and finding decane, using better GPC equipment.

Two kinetic runs were made and the data plotted. The Grignard concentration was seen to vary in a random manner between the limits of 0.071 M and 0.068 M for the first and 0.051 M and 0.049 M for the second run. This suggested that either no reaction was taking place, or that another titratable species was influencing the Grignard determination.

At this point analyses were made by GPC before and after catalyst addition in order to determine initial coupling and catalyst effect. GPC data of hydrolyzed Grignard indicated the presence of pentane, ether, amyl bromide and decane. Pentene was detected partially resolved from pentane in subsequent experiments. The corresponding GPC plots of Grignard after addition of an ethereal solution of catalyst showed no appreciable change in the relativ e amounts of the components, i.e., no noticeable reaction had occurred. It was then recalled that in an early check for Grignard yield, GPC analyses before and after the

[21] R. L. Whittaker, Unpublished Master's Thesis, U.S. Naval Posgraduate School, 1964.

addition of solid $CoBr_2$ directly to the three-necked flask (i.e., Mg also present) showed a marked amount of coupling. This increase in the amount of decane was shown to be accompanied by a corresponding decrease in the amount of amyl bromide.

Effort was shifted to the hexyl system in which complete resolution of the hexyl bromide and dodecane GPC peaks afforded quantitative data which were not realized in the amyl case. Inspection of the data presented in Tables I through III leads to the following observations: (1) formation of Grignard in THF is accompanied by disproportionation, whereas the synthesis in ether is not, (2) addition of catalyst in the solid form to ethereal Grignard results in disproportionation, (3) addition of catalyst in solid or solution form to the THF or ether system does not result in additional coupling product. A reaction with Grignard, halide, and $CoBr_2$ all dissolved in THF with solid magnesium present (run no. C6-3) also gave no additional coupling. However, data from HBr treatment, intended to measure the amount of disproportionation, were invalidated by an unexplained increase in the hexane/hexene peak. The GC-4 analysis of run C6-6 for hexane, hexene and ether after the addition of magnesium (see Table II, note 5) detected no hexane or hexene. No weight was given to this unexplained observation.

No attempt was made to correlate the amount of catalyst added versus the product distribution, nor to determine the fate of the cobalt.

It is concluded that (1) the reports of Kharasch reactions in the literature have overlooked the importance of a heterogeneous versus homogeneous system and have discussed mechanism without regarding the aromatic or aliphatic nature of reactants, (2) most reports in the literature have not analyzed the initial Grignard solution for coupling

product and, hence, failed to distinguish between overall yield and yield due to the catalyst, (3) coupling in aliphatic systems apparently requires the presence of magnesium and catalyst in the solid form, (4) disproportionation in aliphatic systems apparently requires the presence of catalyst in the solid form.

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13. ABSTRACT

The reaction between hexylmagnesium bromide and hexyl bromide, catalyzed by cobaltous bromide is studied in ether and in tetrahydrofuran. The corresponding reaction of amyl Grignard in ether is also studied. Analysis of organic products was by gas partition chromatography and by titration of hydrolyzed Grignard. The observations are discussed relative to prior work, particularly noting the significance of the physical state of the catalyst and the nature of the organic moeity.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Organometallic						
Grignard						
Cobalt						

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